TBA Treatment and Discharge Issues

Site Assessment and Mitigation Forum
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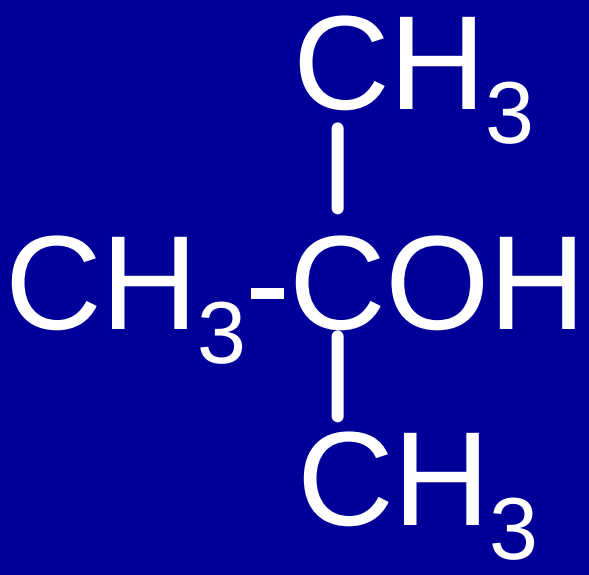
Tert-Butyl Alcohol - TBA



Goals of Corrective Action

- Protect People and the Environment
- Focus on Risk Reduction

Current Discharge Limits for TBA

Regional Water Quality Control Boards (RWQCB) are including TBA limits in new general NPDES discharge permits for petroleum site remediation systems.

- Central Coast – 12 ppb limit
- Santa Ana- 12 ppb limit
- LA – 12 ppb limit
- SF Bay – 5 ppb trigger
- Colorado River – 12 ppb trigger

Source of the 12 ppb Discharge Limit

- 12 ppb is the DHS drinking water Action Limit based on an "expedited" risk assessment prepared by OEHHA in 1999.
- A 10^{-6} based risk based on the assumption that one consumes 2 L a day for 70 years.
- CA Prop 65 uses 10^{-5} risk, which would change the 12 ppb action level to 120 ppb
- USEPA Region 9 has published health-based tap water criteria for two similar butyl alcohols (n-butanol and isobutyl alcohol) of 3600 and 1800 ug/L, respectively

Is a 12 ppb limit needed to protect people and the environment?

- Action Limit based on conservative drinking water assumptions.
- Assumes direct linkage between discharge and drinking water
- Ignores low flow, temporary nature of treatment systems
- Ignores system variability – set as maximum allowable, not time based average.

TBA Risk Issues

Cancer Slope factor used to calculate 12 ppb but:

- Not classified as a carcinogen by EPA, IARC, NTP, OSHA, CA Prop65, ACGIH
- National Toxicity Program (NTP) bioassay cited in OEHHA memo showed no clear evidence of carcinogenicity
- TBA not listed in OEHHAs list of Public Health Goals or their Toxicity Criteria Database

TBA Eco-Risk Issues

- Aquatic LC_{50} >2,000,000 ppb
- Research by the USGS suggests rapid degradation of TBA by microorganisms in surface water sediments

Verschueren, 1996

Technical Concerns with the TBA Limit

- Analytical Issues
- Limited remedial options
- Increased size & complexity of treatment systems
- Higher frequency of downtime
- Increased risk of violation

May Result in Delays in Remediation

ANALYTICAL ISSUES

Even if TBA can be detected at 10 ppb in clean water, it can not be accurately measured at 12 ppb in real samples.

- Practical Quantification Limit typically 5-10x the detection limit.
- Reported detection limits range from 1 ppb - 2,000 ppb.
- DLs highly dependent on other contaminant levels
  - Labs typically dilute samples based on highest concentration constituent.
  - Most common DL $\geq$ 50 ppb.

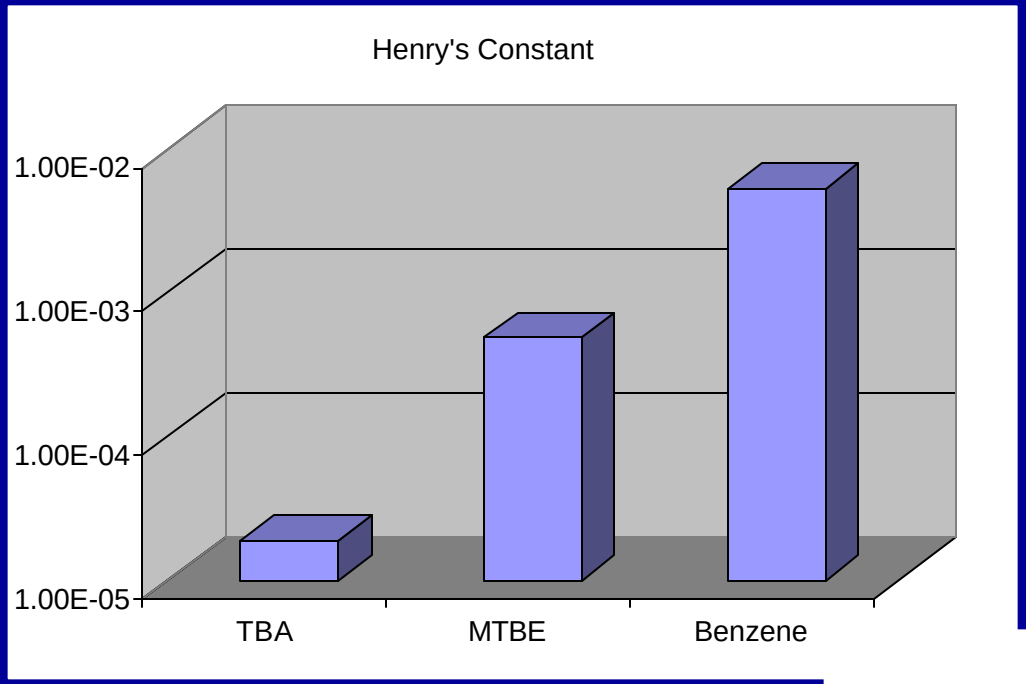
ANALYTICAL ISSUES

Standard methods were developed for non-polar VOCs not highly soluble alcohols

- Poor purging efficiency- leads to inconsistent results.
- Poor separation on GC column- leads to false positive caused by other polar compounds.
- Poor detector response results in higher uncertainty.
- Hydrolytic breakdown of MTBE to TBA during analytical process (EPA 2002) leads to false positive.

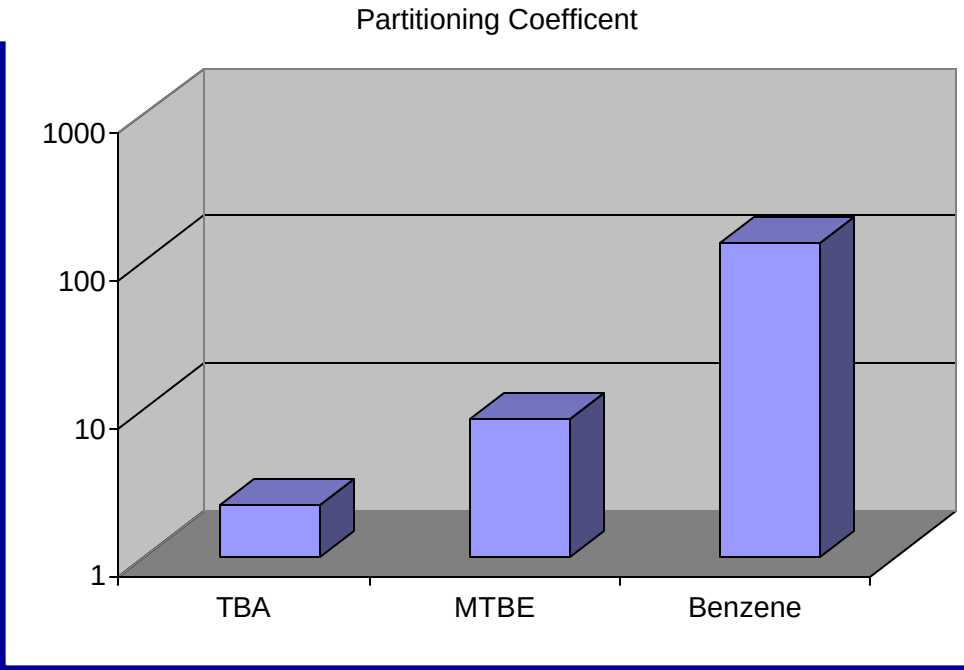
Technical Challenges of TBA Treatment

- TBA chemical characteristics and their impacts on treatment efficacy
- Groundwater treatment technologies:
  - air stripping,
  - carbon adsorption
  - biotreatment



Henry’s Law controls volatilization

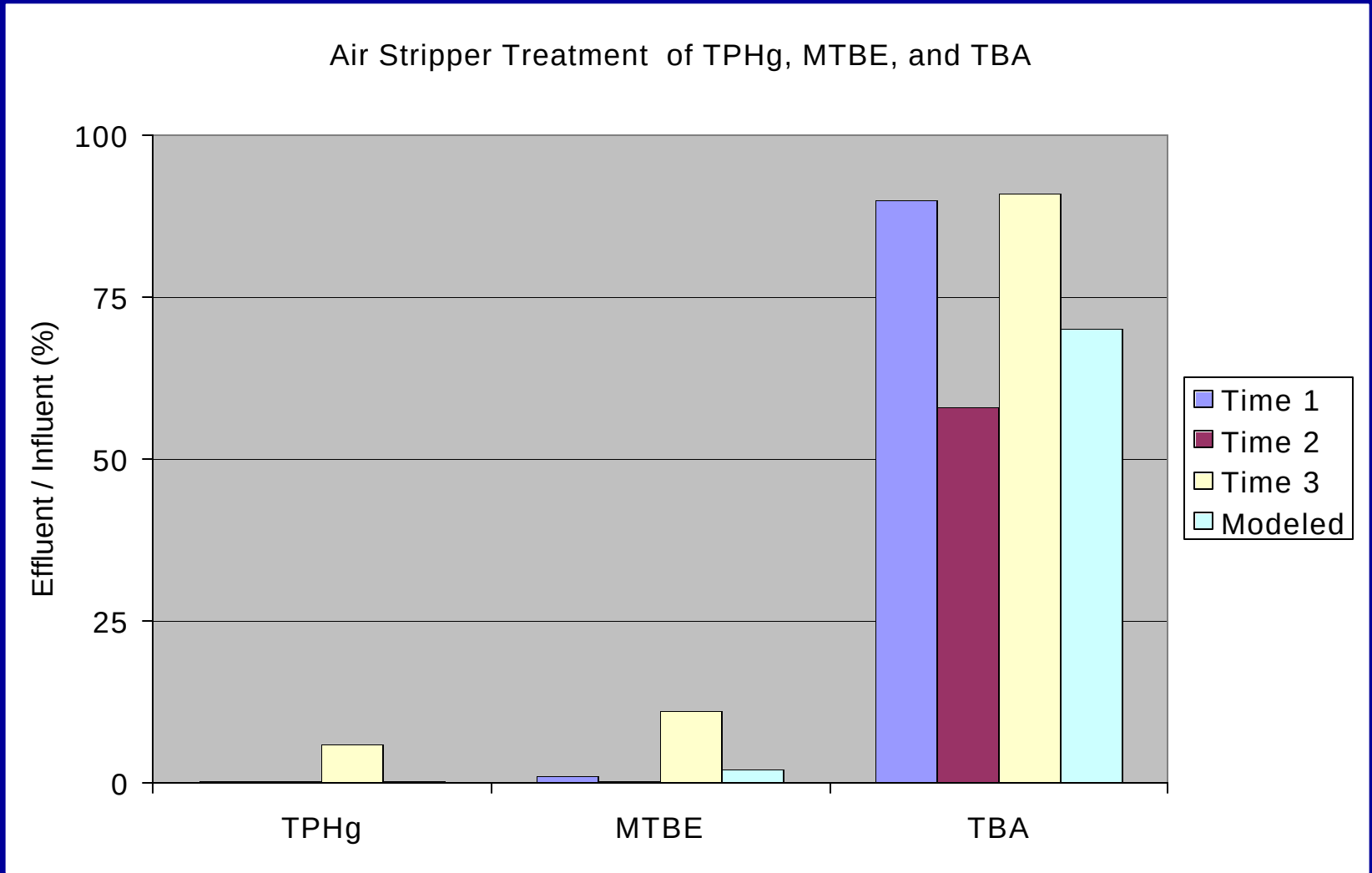
The Partitioning Coefficient controls sorption to carbon



Air Stripping efficiency is related to Henry's Constant

The expected stripping efficiency is

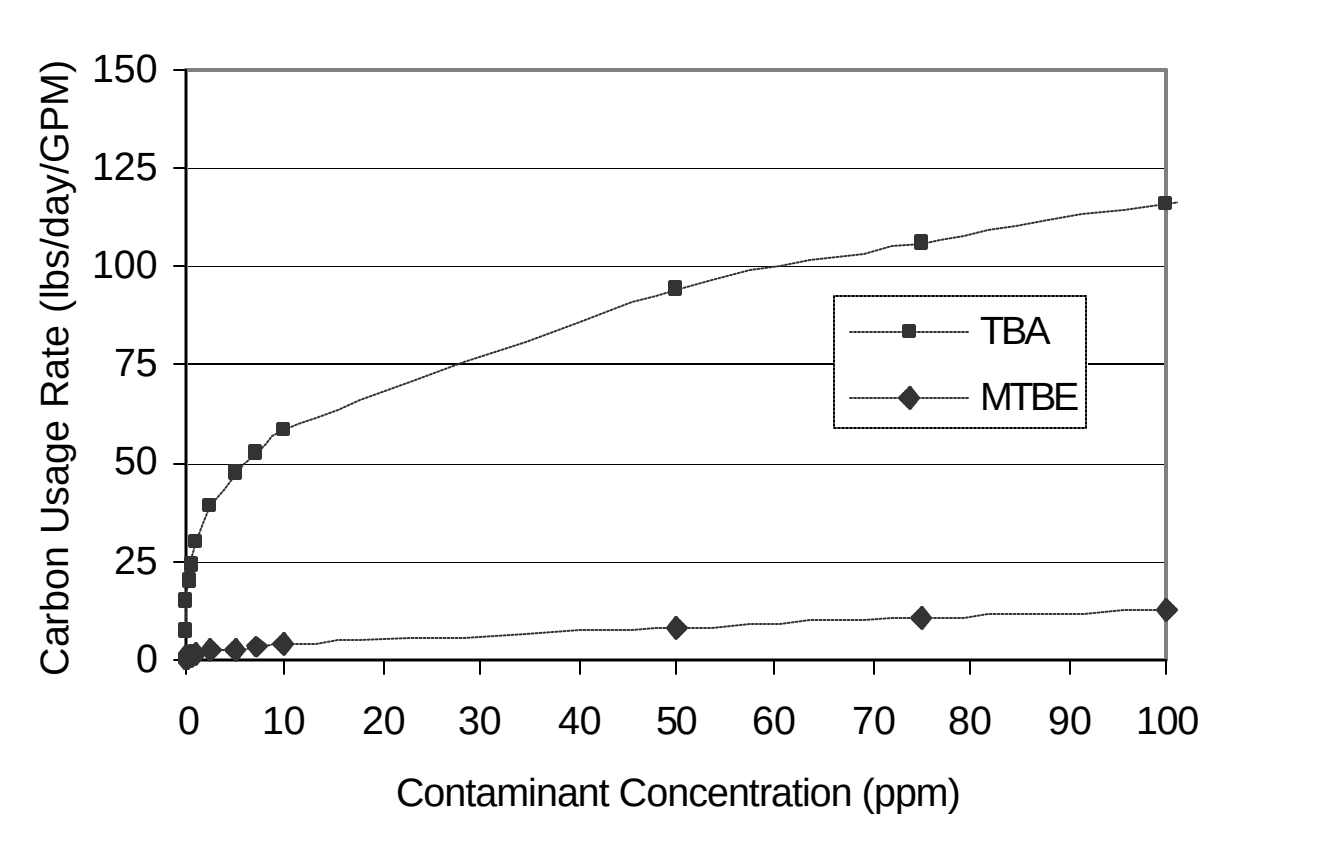
Hydrocarbon > MTBE >> TBA



Adsorption by Granular Activated Carbon

- Carbon has limited capacity for adsorption of TBA.
- TBA GAC system will require a higher number of larger canisters.
- Change out rate may be days to weeks.
- TBA is easily desorbed by competing compounds which leads to occasional spikes in effluent concentration.

TBA is not effectively treated with GAC



At low concentrations it can take 50x as much carbon to treat TBA then treat the same amount of MTBE.

(Based on information from Calgon and Westates Carbon)

Biotreatment of TBA

- While biotreatment shows promise as a process for the treating TBA in groundwater, there is little experience running bioreactors at pump and treat sites.
- While both bioaugmentation and natural inoculation have been used, there is often an extended start-up time.
- Bacteria growing on other gasoline constituents can out compete TBA degraders.
- There are periodic peaks in the effluent stream which can not be attributed to abnormal operations.

Biotreatment Operations

- Most sites have low dissolved oxygen content in the groundwater. Need to aerate water can result in vapor phase treatment requirements.
- System performance can be severely affected by the loss of oxygen source, interrupted feed, and/or variable influent concentration.
- Not always possible to identify reasons for loss of activity.
- High concentration of organic or Fe in the feed stream can result in high pressure drop in the bed. Backwashing the BioGAC bed has a negative effect on the reactor performance.

Evaluation of Oxygenate Remedial Technologies

- A number of oil companies have internal efforts focused on better understanding the remedial options for oxygenates.
- Joint Industrial groups such as API and WSPA support a number of projects evaluating treatment options.

ChevronTexaco MTBE Remediation Technology Demonstration Program

- In Situ Remediation
  - Source Zone (multi-phase extraction, soil vapor extraction)
  - Dissolved plume (sparging, biobarriers, in-situ oxidation)
- Ex Situ Treatment
  - Air Strippers
  - GAC
  - Bioreactors
  - Chemical Oxidation

An Increased Focus on TBA in 2002

WSPA TBA Treatment Evaluation

Project Goals

- Develop data to support setting a technology based discharge limit.
- Improve understanding of TBA treatment options

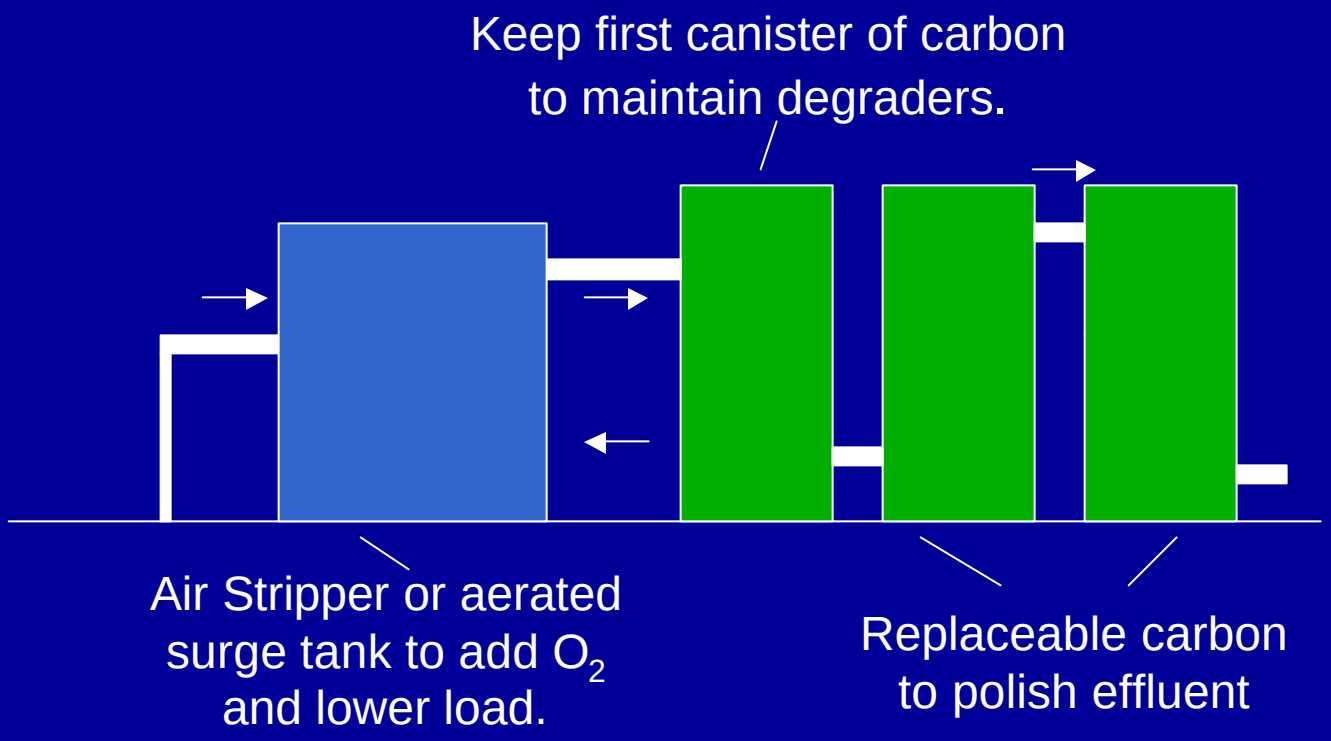
WSPA is working with the Santa Ana Regional Water Quality Control Board

WSPA TBA Treatment Evaluation

- Over 20 sites participating.
- Variety of technologies- Stripper, GAC, BioGAC, Bioreactors, Advance Oxidation
- Range of influent concentrations and flow rates
- Increased monitoring frequency to better understand operations and variability in treatment efficacy.

API Oxygenate Research Program

Operations Manual for BioGAC Systems for TBA Treatment - Due out 1st Quarter 2003



Conclusion

- A maximum allowable concentration of 12 ppb is not required to protect people and environment at most sites.
- Consistent with the EPA NPDES Permit Writer's Guide, permit limits should consider system variability.
- New limits may delay remediation.
- Industry is working to improve our understanding of TBA treatment options.